

PROCESS FOR MAKING ALLYL SUCCINIC ANHYDRIDE

CROSS-REFERENCE TO RELATED APPLICATIONS

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This application claims priority from U.S. provisional patent application No. 60/461,878.

FIELD OF THE INVENTION

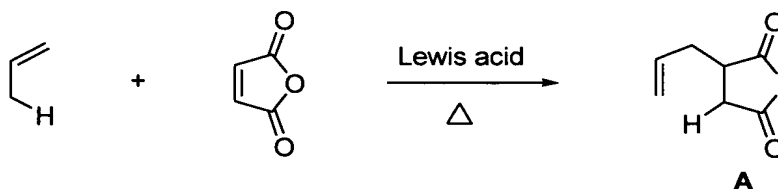
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This invention relates a process for making allyl succinic anhydride.

BACKGROUND OF THE INVENTION

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Allylsuccinic anhydride can be made by a Lewis Acid catalyzed ene reaction between maleic anhydride and propene according to reaction scheme 1 below:



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Reaction Scheme 1

AlCl₃ catalyzes the reaction efficiently but requires harsh conditions (T = 200°C). However, the anhydride undergoes exothermic polymerization at 205°C. For safety reasons, the industrial process should be performed 30°C below the polymerization reaction. However, in these conditions, AlCl₃ is not an efficient catalyst.

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The ene reaction is the reaction of an alkene having an allylic
hydrogen (ene) with a compound containing a double or triple bond
5 (enophile) to form a new bond with migration of the ene double bond
and 1,5-hydrogen shift.

Since the enophile, like the dienophile in a Diels-Alder reaction,
should be electron deficient, complexation of Lewis acids to enophile
10 containing basic groups promotes the ene reaction. See Snider, B.B.
Acc. Chem. Res. **1980**, 13, 426. The choice of the Lewis acid
depends upon the enophile to be used. Some of them require very
acidic Lewis acids, others require milder ones. Some examples of
Lewis used for the ene reactions are: AlCl_3 , EtAlCl_2 , Me_2AlCl , BF_3 ,
15 SnCl_4 , TiCl_4 , FeCl_3 , ZnCl_2 .

In the literature, the ene reaction between propene and maleic
anhydride is described without catalyst but at a high temperature
(200-250°C). See (a) Alder, K.; Pasher, F.; Schmitz, A. *Chem. Ber.*
20 **1943**, 76, 27. (b) Phillips, D.D.; Hill, T.J. *J. Am. Chem. Soc.* **1958**,
80, 3663. (c) Anderson, et al., 1966, U.S. Patent No. 3,243,480.

U.S. Patent No. 3,819,660 discloses the reaction of an alkene
such as propene with maleic anhydride to produce an alkenyl succinic
25 anhydride. That patent teaches the use of a mixture of para-toluene
sulfonic acid and acetic anhydride as a catalyst.

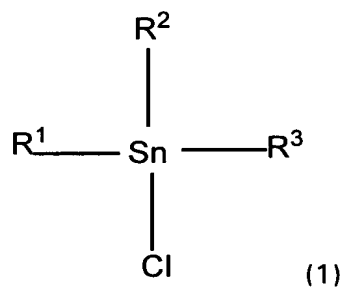
SUMMARY OF THE INVENTION

This invention is directed to a process for making allyl succinic
5 anhydride, comprising reacting propene with maleic anhydride in the
presence of a catalytic amount of alkyl tin chloride catalyst.

DETAILED DESCRIPTION OF THE INVENTION

10 The term "catalytic amount" is recognized in the art and means
a substoichiometric amount of catalyst relative to a reactant. As used
herein, a catalytic amount is typically in the range of from about 1.0×10^{-6} to about 0.9 mole catalyst per mole of maleic anhydride.

15 The catalysts useful in the process of the present invention are
organotin chloride catalysts. Suitable organotin chloride catalysts are
those according to formula (1) below:



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wherein

R^1 , R^2 are each independently alkyl, alkenyl, alkynyl, or phenyl,
 R^3 is Cl or alkyl, alkenyl, or alkynyl.

25 As used herein, "alkyl" means a saturated hydrocarbon,
including, straight or branched saturated hydrocarbon chains such as
methyl ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 1,1-

dimethylethyl, hexyl, octyl, decyl, dodecyl, stearyl, and saturated hydrocarbon rings, such as cyclohexyl and cyclooctyl. As used herein, "alkenyl" means a straight or branched hydrocarbon chain having one or more carbon-carbon double bonds, such as for example, ethene, propene, 1-butene, 2-butene, propadiene. As used herein, "alkynyl" means a straight or branched hydrocarbon chain having one or more carbon-carbon triple bonds, such as, for example, ethyne, propyne, butadiyne, 1,4-hexadiyne. As used herein, "phenyl" means an aromatic ring of six carbon atoms, which may optionally be substituted on one or more carbons of the ring with hydrocarbon groups, including, for example, alkyl, alkenyl, and alkynyl groups

In one embodiment, R^1 and R^2 are each independently (C_1 - C_6)alkyl or phenyl and R^3 is Cl or (C_1 - C_6)alkyl. As used herein, "(C_1 - C_6)alkyl" means a straight or branched alkyl group having from 1 to 6 carbon atoms per group, such as, for example, methyl, ethyl, propyl, 1-methylethyl, butyl, 1-methylpropyl, 1,1-dimethylethyl, 2,2-dimethylpropyl, 1,1-dimethylpropyl, or hexyl, 4-methylpentyl.

Suitable organotin chloride catalysts include methyl tin dichloride, dimethyl tin dichloride, ethyl tin dichloride, diethyl tin dichloride, n-butyl tin trichloride, di-n-butyl tin dichloride, s-butyl tin dichloride, di s-butyl tin dichloride, t-butyl tin dichloride, di t-butyl tin dichloride, n-pentyl tin trichloride, di n-pentyl tin dichloride, n-hexyl tin trichloride, di n-hexyl tin dichloride and phenyl tin dichloride.

The process of the present invention is useful at temperatures below the temperature at which competing reactions, such as polymerization reactions and/or decomposition reactions, become problematic. In one embodiment, the reaction according to the process of the present invention is carried out at temperatures below

about 200°C, more typically below about 180°C, and even more typically from about 155°C to about 175°C.

In one embodiment, the reaction mixture initially comprises
5 substantially equimolar amounts propene and maleic anhydride. In an alternative embodiment, the reaction mixture initially comprises a molar excess, typically up to about 10 mole %, of propene relative to the amount of maleic anhydride.

10 The reaction is typically carried out in a solvent such as, for example, a hydrocarbon, more typically an aromatic hydrocarbon such as toluene, that is, inert under the anticipated reaction conditions. The amount of solvent may vary widely. An amount of from about 0.1 to about 10 parts by weight ("pbw") solvent per pbw maleic
15 anhydride is typically used. More typically an amount of from about 0.5 to about 1.5 pbw solvent per pbw maleic anhydride is used.

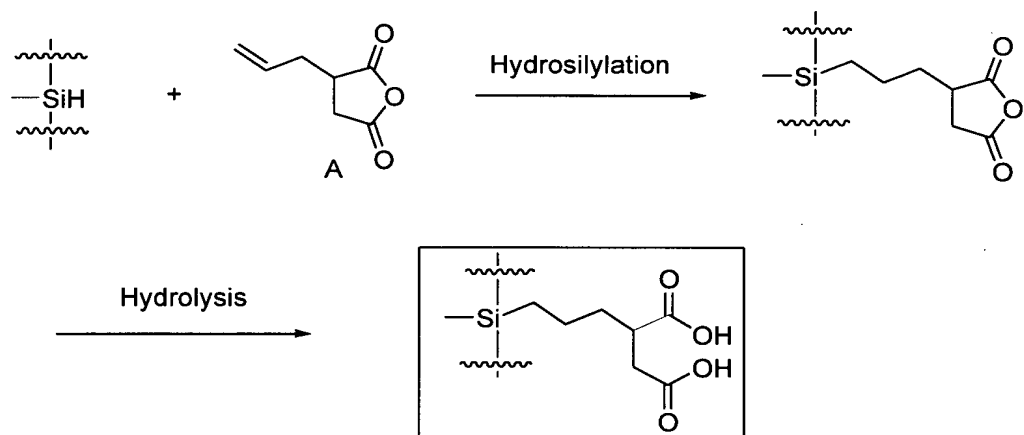
In one embodiment, the process of the present invention is conducted at a pressure of from about 100 to about 10,000 pounds
20 per square inch above atmospheric pressure ("psig"), typically from about 100 to about 1,000 psig, and more typically from about 100 to about 800 psig.

The reaction is typically carried out in the presence of a free
25 radical scavenger, such as, for example, methoxyphenol, to inhibit polymerization of the maleic anhydride reactant and the allyl succinic product.

The allyl succinic anhydride product is useful for a variety of
30 purposes, such as for example, as a corrosion inhibitor.

Homopolymers and copolymers of a similar monomer are known to those skilled in the art to be useful in corrosion inhibitors, as disclosed in U.S. Patent No. 4,317,744 to Levi entitled "Corrosion Inhibitors".

5 In one embodiment, the ally succinic anhydride is used to form a hydrosilylated diacid product according to Reaction Scheme 2 below, wherein the ally succinic anhydride is grafted to a silicone oil via a hydrosilylation reaction and hydrosilylation product is then hydrolysed to form a diacid product. The diacid product is useful as a
10 corrosion inhibitor.



Reaction Scheme 2

The hydrosilylated diacid product is useful as a corrosion
15 inhibitor

Example 1

A screening of Lewis acids as catalysts for the ene reaction
20 was performed in a Top reactor (25mL). Maleic anhydride, methoxyphenol (polymerization inhibitor), Lewis acid and solvent (anhydrous toluene) were introduced under argon into the reactor. Then, the reactor was cooled in dry ice/acetone bath and the propene

was added. The relative amounts of the materials used are given in the following table.

Reactant	MW (g/mol)	Eq.	n (mmol)	m (g)
Maleic anhydride	98.06	1	41	4
4-Methoxyphenol	124.14	0.02	0.8	0.1
Lewis acid		0.05	2	
Propene	42.08	2.3	95	4
Toluene				4mL

The reaction mixture was stirred for 12 hours at a given
5 temperature. Finally, the reaction mixture was analyzed by IR spectroscopy.

First, the reaction conditions and the qualitative IR method
were validated by a reference experiment with AlCl_3 as a catalyst at
10 200°C . Then, a screening of the 38 typical Lewis acids listed below (wherein "acac" means acetyl acetonate) as the catalyst for the reaction was conducted using the same procedure, except at a temperature of 150°C .

AlBr_3	$\text{Co}(\text{acac})_3$	K_2PO_4	$\text{Ti}(\text{OiPr})_4$
AlCl_3	CsCl	$\text{Mn}(\text{phtalocyanin})$	TiCl_4
$\text{AlCl}_3/\text{CsCl}$	$\text{Cu}(\text{acac})_2$	$\text{Mo}(\text{C}_5\text{H}_5)_2\text{Cl}_2$	$\text{Ti}(\text{C}_5\text{H}_5)_2\text{Cl}_2$
$\text{AlCl}_3/\text{NaCl}$	CuCl	NbOCl_2	$\text{V}(\text{C}_5\text{H}_5)_2\text{Cl}_2$
AlI_3	DyCl_3	$\text{Nd}(\text{Otf})_3$	WCl_4
AlMe_3	$\text{Fe}(\text{acac})_2$	$\text{Ni}(\text{acac})_2$	$\text{Zr}(\text{C}_5\text{H}_5)_2\text{HCl}$
AsPh_3	FeCl_3	$\text{Rh}(\text{TFA})_2$	$\text{Zr}(\text{C}_5\text{H}_5)_2\text{Cl}_2$
BBr_3	$\text{Fe}(\text{C}_5\text{H}_5)_2$	SePh_2Cl_2	ZnF_2
$\text{B}(\text{amyl})_3$	GeI_4	SnBuCl_3	

The IR spectra demonstrated that none of the reactions at 150°C using the Lewis acid compounds produced the desired product.

AlCl₃, HfCl₃, ZrCl₂, CdI₂, and Me₂SnCl₂ were then tested at 200°C. HfCl₃ and ZrCl₂ did not give the expected product, whereas in the presence of Me₂SnCl₂ or CdI₂, the product is observed by IR spectroscopy. But as mentioned before, this temperature is likely too high for an industrial process.

Then, a targeted screening of tin compounds was performed at 175°C. The results are given in the following table (+ :product; - : no product):

Catalyst	IR qualitative result
Me ₂ SnCl ₂	+ + +
<i>n</i> -Bu ₂ SnCl ₂	+ +
<i>n</i> -BuSnCl ₃	+
SnCl ₄	-
Ph ₃ SnCl	-

The three catalysts Me₂SnCl₂, *n*-BuSnCl₂ and *n*-BuSnCl₃ were active in the formation of the allylsuccinic anhydride. Me₂SnCl₂ was the most efficient.

Considering these results, we may consider that an efficient catalyst for this reaction should have intermediary acidity. Thus, the acidity of tin Lewis acids has been evaluated by calculating their respective Lowest Unoccupied Molecular Orbital ("LUMO") energies

Tin compound	E Lumo	Activity
Tin tetrachloride	-96.16	Inactive
n-butyl tin trichloride	- 71.2	Active
Diphenyl tin dichloride	- 51.81	Not tested
Divinyl tin dichloride	- 51.04	Not tested
Dimethyl tin dichloride	- 50.12	Active
Di n-butyl tin dichloride	- 48.74	Active
Di t-butyl tin dichloride	- 48.37	Not tested
Triphenyl tin chloride	- 28.52	Inactive

The results suggest a relationship between catalytic activity and LUMO energy of the compounds. The three active Lewis acids tested each have a LUMO energy between -40 and -80 kcal/mol, whereas neither a stronger Lewis acid (SnCl_4 , $E_{\text{LUMO}} = -96.16$ kcal/mol), nor a weaker Lewis acid (Ph_3SnCl , $E_{\text{LUMO}} = -28.52$ kcal/mol) catalyzed the ene reaction.

10 Example 2

A Parr reactor (2L) was charged with 300g maleic anhydride (3.06 moles), 300g toluene, 10g dimethyl tin dichloride, and 138 g propene (1.1 molar equivalents, based on maleic anhydride). The temperature of the reaction mixture was increased to 175°C. At this temperature the pressure within the reactor was 634 psig. The reaction mixture was stirred at 200 rpm with a gassing stirrer. The pressure dropped substantially linearly through the reaction, indicating propene consumption. After 48 hours of heating, the pressure within the reactor was 412 psi.

The reaction mixture was cooled to yield a clean, polymer free liquid. Solvent was removed using a rotary evaporator to provide a liquid product comprising of 59% maleic anhydride, and 41% allylsuccinic anhydride (by NMR).